

XANES features in fluoromethanes and electronegativity

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Abstract : The near edge features in the K -absorption spectra of carbon in methane vapour, fluoromethanes and carbon tetrafluoride have been reported by F C Brown, R Z Bachrach and A Bianconi (1978). The transitions assigned by them to these features have been tested by us by plotting their energies against $\sum_i (\chi_c - \chi_l)$, where χ_c and χ_l are the electronegativities of the carbon and the ligand atoms respectively. We obtain linear plots which help us in confirming the assignments in doubtful cases. Besides this, we have been able to suggest assignments in a few cases, where they have not been given by Brown *et al*

Keywords : XANES, electronegativity, fluoromethanes

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Introduction

It is well known that the X-ray absorption discontinuities exhibit certain features within and near the main edges [1]. The different features which commonly constitute XANES (X-ray Absorption Near Edge Structure) are known to be sensitive to chemical environment of the absorbing atom [2]. In the present article, an attempt is being made to see if the electronegativity values could be used to systematize the XANES features of the carbon K -absorption discontinuity in methane, fluoromethanes and carbon tetrafluoride.

2. The carbon K edge XANES features in methane and fluoromethanes

The study of the carbon K -edge has received the attention of X-ray spectroscopists [3,4] for a long time, probably because carbon plays a very important role in chemistry and life processes. The K -absorption spectrum of methane reported by Chun [5] provided the first example of a K -shell spectrum from an organic compound obtained with synchrotron radiation. Chun's spectrum of CH_4 together with electron impact excitation spectra [6,7]

have been discussed extensively in comparison with theoretical calculations [8,9]. Brown *et al* [10] later reported the soft X-ray absorption spectra of carbon in CH_4 , CH_3F , CH_2F_2 , CHF_3 and CF_4 gases using the synchrotron radiation facility at Stanford. They were able to obtain the XANES features in these gases, inspite of the great experimental difficulties involved in recording these spectra, which lie in the wavelength region of 43.7 \AA (about 284 eV). They obtained four XANES features for CH_4 , five for CH_3F , six for CH_2F_2 and CHF_3 , and seven features for CF_4 . The energies of these features are given in the Table 1.

Table 1. XANES features and their assignments.

Molecule	Spectral feature [10]	Energy [10] (eV)	ΔE [10] (eV)	$\sum_i (\chi_i - \chi_p)$	Orbital assignment [10]	Our assignment
CH_4	1	287.0	3.8	5.76	$3a_1 (3s)$	$3s$
	2	288.1	2.7		$3t_2 (3p)$	$3p$
	3	289.4	1.4		$nt_2; n \geq 4$	np
	4	290.8 [12]	0.0		ionization	ionization
CH_3F	1	289.1	4.4	2.71	$3s$	$3s$
	2	290.5	3.0		$3p$	$3p$
	3	291.6	1.9		$3d$	$3d$
	4	292.0	1.5		np	np
	5	293.5 [13,15]	0.0		ionization	ionization
CH_2F_2	1	291.9	4.5	-0.34	$3s$	$3s$
	2	292.9	3.5		—	$3p$
	3	294.0	2.4		$3p$	—
	4	294.5	1.9		$3d$	$3d$
	5	295.5	0.9		np	np
	6	296.4 [13,15]	0.0		ionization	ionization
CHF_3	1	294.8	4.3	-3.39	—	$3s$
	2	295.3	3.8		—	$3p$
	3	297.2	1.9		$3d ?$	$3d$
	4	298.0	1.2*		—	—
	5	298.6	0.5		—	$np (n \geq 4)$
	6	299.1 [13,15]	0.0		ionization	ionization
CF_4	1	297.6	4.2	-6.44	—	$3s$
	2	298.0	3.8		—	$3p$
	3	298.5	3.3		—	—
	4	298.9	2.9		—	—
	5	299.9	1.9		$3d ?$	$3d$
	6	301.0	0.8		np	np
	7	301.8 [13,15]	0.0		ionization	ionization

* This value should actually be 1.1 (299.1–298.0) eV. This may be a printing mistake in the paper of Brown *et al* [10].

Some of the XANES features are well resolved while some features are not so well distinguishable. We note that as one proceeds from methane through the fluorinated compounds, the feature 1 steepens and finally merges with feature 2 in the complex spectrum of CF_4 . In each spectrum, these workers have identified a feature which is supposed to correspond to the ionization energy of the system reported by different workers [11–15]. All the preceding XANES features are then attributed to the transitions of the 1s core electron of carbon to the available outer states.

In the case of CH_4 , the molecular orbital diagram is well known. The relatively intense peak at about 288 eV [7,9] (feature 2 as reported by Brown *et al* [10]) was assigned to the $1a_1(1s) \rightarrow 2t_2(3p)$ Rydberg transition [5,6]. The earlier weaker peak (feature 1 reported by Brown *et al* [10]) has been attributed by Bagus *et al* [9] to the $1a_1(1s) \rightarrow 3a_1(3s)$ Rydberg transition which is formally electric dipole forbidden but is observed because of vibronic coupling. They state that the lowest energy dipole allowed Rydberg state is represented by the configuration $1a_1 2a_1^2 1t_2^6 2t_2$, where the $2t_2$ molecular orbital is predominantly a 3p carbon orbital.

Brown *et al* [10] attributed the feature 1 to the $3a_1$ molecular orbital and the feature 2 to the $3t_2$ orbital*. However, since the MO diagrams for the fluoromethanes are not available, Brown *et al* had to assign the XANES features in these molecules to the atomic orbitals 3s, 3p, 3d, np etc. of carbon. In the case of CF_4 , Wight and Brion [6] state that the first four features can hardly be identified with the Rydberg like s and p transitions of CH_4 .

The final orbitals corresponding to XANES features as given by Brown *et al*, are indicated in the column 6 of the table. It will be seen that in several cases, they have not been able to assign the orbitals and in some cases they were in doubt about the assignments as is reflected from the question marks put by them.

3. The application of electronegativity

It is well known that many physicochemical properties of molecules depend upon the electronegativity values of their constituent atoms [16]. The application of electronegativity values to interpret the chemical shifts in NMR [17], photoelectron [13] and X-ray absorption [18] spectroscopies is well known. Recently, the present authors [19,20] have shown that the rotational constants of diatomic halides depend upon the electronegativity differences of the constituent atoms. To our knowledge, the systematization of XANES features with the help of electronegativity values has not been reported so far.

In order to see the direct effect of ligands on the different XANES features in fluoromethanes, we have calculated the values of $\sum (\chi_c - \chi_l)$ where χ_c is the electronegativity value of the carbon atom, χ_l that of the ligand atom and the summation is carried over all the ligands as has been done earlier by Mande *et al* [21]. The values of

* We feel that $3t_2$ is a printing mistake in the article of Brown *et al*. It should be $2t_2$ as shown earlier by Bagus *et al* and Hitchcock *et al*.

$\Sigma(\chi_c - \chi_l)$ for CH_4 , CH_3F , CH_2F_2 , CHF_3 and CF_4 using the electronegativity values on the scale of Mande and coworkers [21–23] are given in column 5 of the table.

In Figure 1 are plotted the energies of XANES features given in column 3 of the table against the values of $\Sigma(\chi_c - \chi_l)$. We obtain five separate straight lines, one for each

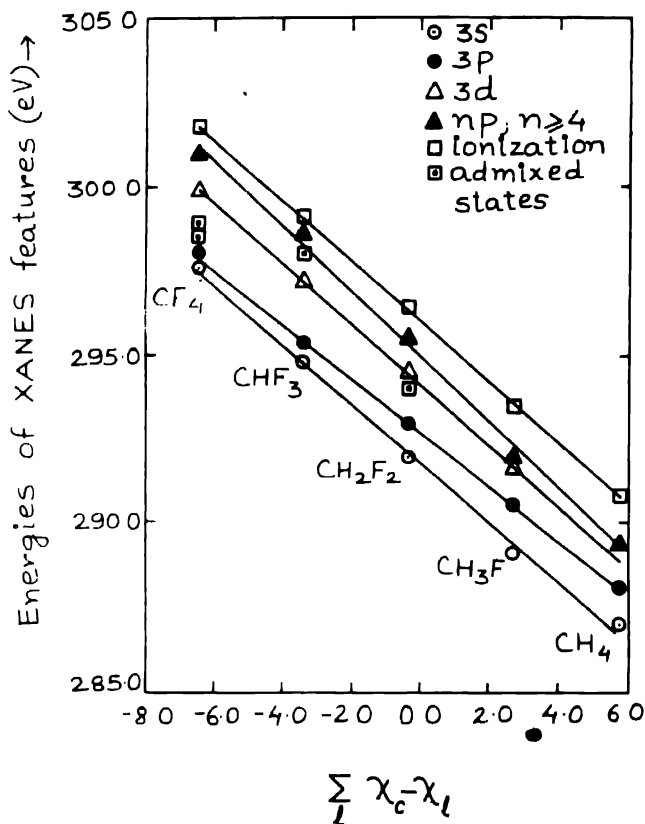


Figure 1. Plot showing the variation between the values of energies of XANES features and $\Sigma(\chi_c - \chi_l)$

feature assigned to a particular orbital. The line 1 corresponds to the feature assigned to the 3s orbital, line 2 to the 3p orbital, line 3 to the 3d orbital, line 4 to np ($n \geq 4$) and line 5 to the feature assigned to ionization. From Table 1 and Figure 1, we observe that :

1. The assignments given by Brown *et al* seem to be correct except in the case of CH_2F_2 where they have assigned the feature 3 (294.0 eV) to the 3p orbital. Our work indicates that the feature 2 (292.9 eV) rather than the feature 3 should be attributed to the 3p orbital in the case of this compound. The feature 3 can be assigned to the admixture of 3p and 3d orbitals, as it lies between the plots for 3p and 3d.
2. As can be seen in the Table 1, Brown *et al* have put question marks against the assignments of feature 3 in the case of CHF_3 and feature 5 in the case of CF_4 . These

features lie very well on the E vs $\sum_i(\chi_c - \chi_i)$ plot for 3d, and hence there does not seem to be any reason to doubt the assignments. We also note that the position of the 3d orbital with respect to the ionization feature remains constant (1.9 eV) in all the fluorinated species.

3. In the case of the CHF_3 molecule, Brown *et al* have not assigned the features 1, 2, 4 and 5 to outer orbitals. Our plots indicate that the features 1 and 2 can be assigned to the 3s and 3p orbitals respectively, and the feature 5 can be assigned to the np ($n \geq 4$) level. The feature 4 lies nearer to the plot corresponding to that of the np orbital and may be assigned to the admixture of 3d and np ($n \geq 4$) states.
4. In the case of CF_4 , the features 1, 2, 3 and 4 have not been assigned by Brown *et al*. Our plots show that the features 1 and 2 can be assigned to the 3s and 3p levels respectively. The features 3 and 4 which lie in between the 3p and 3d plots, can be assigned to the states which are admixtures of these orbitals.

Our work thus shows that the electronegativity values of the constituent atoms can be helpful in systematizing the experimental data on XANES of polyatomic molecules.

5. Concluding remarks

Unfortunately, no experimental X-ray absorption work seems to have been carried out on the other halomethanes. It may be worthwhile to study the XANES spectra of other halomethanes, carbon tetrahalides and other polyatomic molecules to see the effects of chemical bonding on the outer orbitals of the carbon atom. With improved resolution of detecting systems now available, more meaningful work can now be undertaken in this field, using synchrotron radiation.

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